Titanium Hydride Formation through Hydrogen Transfer from 2-Methylpyridine to a Titanium Fulvene Compound; the First Structurally Characterized Terminal Titanium Hydride

Pattiasina, Johannes W.; Bolhuis, Fré van; Teuben, Jan H.

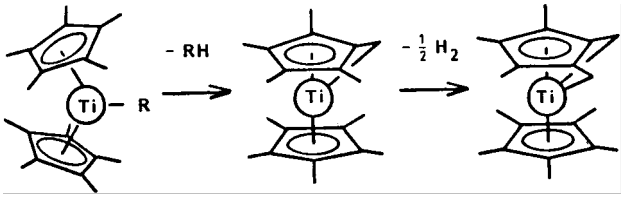
Published in:
Angewandte Chemie International Edition in English

DOI:
10.1002/anie.198703301

Titanium Hydride Formation through Hydrogen Transfer from 2-Methylpyridine to a Titanium Fulvene Compound; the First Structurally Characterized Terminal Titanium Hydride

By *Johannes W. Pattiasina, Fré van Bolhuis,* and *Jan H. Teuben**

In a study of the thermolysis of compounds of the type $[Cp^*_2TiR]$ ($Cp^* = \eta^5$-C_5Me_5; R = H or alkyl), we observed stepwise hydrogen abstraction from one of the Cp* ligands.[1]



We are currently focusing our attention on the reactivity of these modified Cp* ligands. In **1** the tetramethylfulvene ligand may be coordinated either as a combined cyclopentadienyl-alkyl ligand, the "tucked-in" mode **A**,[2] or as a neutral conjugated triene **B**.[3]

In a series of exploratory studies with a variety of substrates with active protons, e.g., acids and alcohols, **1** reacted as a cyclopentadienyl-alkyl complex with transfer of hydrogen from the substrate to the fulvene ligand, thus restoring the original Cp* ligand.[4]

A completely different and unprecedented reaction took place when **1** was exposed to pyridine derivatives. At -80°C the dark purple **1** reacts quickly with 2-methylpyridine in Et_2O to give a dark green solution, which changes to an intense dark blue on warming to room temperature. Concentration and cooling of the solution to -30°C resulted in the formation of beautiful dark blue crystals of **2**.[5]

[*] Dr. J. H. Teuben, Dr. J. W. Pattiasina, F. van Bolhuis
Department of Chemistry, University of Groningen
Nijenborgh 16, NL-9747 AG Groningen (The Netherlands)

$$[Cp^*(C_5Me_4CH_2)Ti] + C_5H_4MeN \xrightarrow{Et_2O}$$

1

$$[Cp^*\{C_5Me_4CH_2(C_5H_3MeN)\}TiH]$$

2

The molecular structure of **2** (Fig. 1)[6] shows that hydrogen transfer from the 6-position of 2-methylpyridine to titanium, concurrent with C-C bond formation between pyridine and the methylene group of the fulvene ligand, has taken place. In this way a Cp* ligand is functionalized with a pyridine ligand to form a chelating ligand.

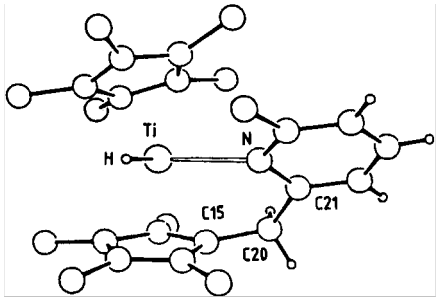


Fig. 1. Molecular crystal structure of $[Cp^*\{C_5Me_4CH_2(C_5H_3MeN)\}TiH]$ **2**.

Compound **2** is the first structurally characterized dicyclopentadienyltitanium hydride with a terminal Ti-H bond. The Ti-H distance (1.70(4) Å) is substantially longer than in other 3d-transition metal terminal hydrides, but comparable with hydrides of the early transition metals of the 4d and 5d series.[7] Until now only structure determinations of titanium hydrides with bridging hydrogen atoms, e.g., complexes containing a Ti-H-Ti, Ti-H-Al, or Ti-H-B structural element, have been published. In these complexes the Ti-H distances vary between 1.69(10) and 1.94(7) Å.[7]

The location of the pyridyl fragment with respect to the Ti atom and especially the Ti-N distance (2.340(3) Å) indicate that we are dealing with a dative Ti-N bond.[8] The angle formed between the Ti atom and the centroids of the substituted cyclopentadienyl rings is 142.7°; the distances between Ti and the centroids (2.086 and 2.064 Å) are close to those found in unsubstituted Cp^*_2Ti derivatives.[9]

The dihedral angle between the plane containing both ring centroids and Ti and the H-Ti-N plane is 91.6°; the H-Ti-N angle is 91(2)°. From this it is clear that **2** has all the characteristics of a regular $Cp^*_2M(L)X$ molecule. The C15-C20 bond deviates slightly from the ring plane (7.4°) toward the metal. The other C(ring)-C(methyl) bonds point away from the metal, thereby producing the normal "dish" shape of the Cp* ligands.[10] The C15-C20-C21 angle (111.5(3)°) shows that C20 is almost perfectly sp^3 hybridized.

The ^{1}H-NMR spectrum of **2**[5] affords assignments of the protons of the cyclopentadienyl ligands. Owing to the paramagnetism of **2**, the signals are broad and shifted strongly. The hydride resonance could not be located, a problem also encountered for the related compound $[Cp^*_2TiH]$.[3] In the IR spectrum, $\bar{\nu}$(Ti-H) is found at 1475 cm^{-1}, slightly lower than for $[Cp^*_2TiH]$. The assignment was confirmed by the synthesis of the deuteride: $\bar{\nu}$(Ti-D) was observed at 1065 cm^{-1} ($\bar{\nu}$(Ti-H)/ $\bar{\nu}$(Ti-D)= 1.38). The ESR spectrum shows a well-resolved doublet, centered at

  0570-0833/87/0404-0330 $ 02.50/0

$g = 1.985$ ($a_H = 11.5$ G), and a clear hyperfine splitting due to interaction with titanium isotopes (^{47}Ti, I = 5/2, ^{49}Ti, I = 7/2, natural abundance 7.28% and 5.51%, respectively, $a_{Ti} = 9.3$ G).

Reaction of **2** with ethylene and DCl also confirmed the presence of a Ti-H functionality.

$$[Ti]H + CH_2{=}CH_2 \longrightarrow [Ti]Et \xrightarrow{D_2} [Ti]D + EtD$$
2 **3** [D]-**2**

$$[Ti]H + DCl \longrightarrow [Ti]Cl + HD$$
2 **4**

$[Ti] = Cp^*\{C_5Me_4CH_2(C_5H_3MeN)\}Ti$

In a Toepler pump controlled experiment, 1 mole of ethylene per mole of Ti was consumed. Compound **3** was isolated as a dark brown, analytically pure crystalline material; it reacts with D_2 to form EtD and [D]-**2** in a 1 :1 molar ratio.[11]

The formation of a Ti-H bond through hydrogen transfer from 2-methylpyridine is completely different from what is regularly observed in reactions with compounds of early transition metals of the type $[Cp_2TiR]$[12] or $[Cp^*_2MR]$ (M = Sc,[13] Y,[14] Lu[15]). In the case of a "tucked-in" bonding mode, metalation of the pyridine with hydrogen transfer to the fulvene ligand and formation of $[Cp^*_2Ti(\eta^2\text{-}C_5H_3MeN)]$ is expected.

A further outstanding feature is the conversion of a fulvene ligand into a functionalized pentamethylcyclopentadienyl group. This reaction may be of considerable synthetic importance as an attractive route to bidentate Cp* ligands.

Experimental Procedure

2: **1** (0.574 g, 1.81 mmol) was dissolved in Et_2O (20 mL) and cooled to -196°C. 2-Methylpyridine (0.168 g, 1.81 mmol) was added and the reaction mixture was warmed to -80°C. Upon gradually warming the mixture to room temperature, the color of the solution changed from red-purple to dark green and finally dark blue. After stirring for 4 h, the solution was filtered, concentrated to 15 mL, and slowly cooled to -30°C to give beautiful dark blue crystals. Yield: 0.335 g (0.82 mmol, 45%) of **2**. Correct elemental analysis.

Received: September 15, 1986;
revised: December 22, 1986 [Z 1931 IE]
German version: *Angew. Chem. 99* (1987) 342

CAS Registry numbers:
1, 53436-87-6; **2,** 107116-24-5; [D]-**2,** 107116-25-6; **3,** 107116-26-7; **4,** 107116-27-8; 2-methylpyridine, 109-06-8.

[1] J. W. Pattiasina, C. E. Hissink, J. L. de Boer, J. H. Teuben, A. Meetsma, A. L. Spek, *J. Am. Chem. Soc. 107* (1985) 7758.
[2] F. G. N. Cloke, J. C. Green, M. L. H. Green, C. P. Morley, *J. Chem. Soc. Chem. Commun. 1985,* 945.
[3] a) J. E. Bercaw, R. H. Marvich, L. G. Bell, H. H. Brintzinger, *J. Am. Chem. Soc. 94* (1972) 1219; b) C. McDade, J. C. Green, J. E. Bercaw, *Organometallics 1* (1982) 1629.
[4] J. H. Teuben in T. J. Marks, I. L. Fragalà (Eds.): *Fundamental and Technological Aspects of Organo-f-Element Chemistry,* Reidel, Dordrecht 1985, p. 195.
[5] ^{1}H-NMR (200.068 MHz, $[D_{10}]Et_2O$ at 0°C; δ values relative to residual protons in the solvent at $\delta = 1.29$; multiplicity, intensity, width at half maximum height (Hz) in parentheses: $\delta = 25.0$ (s, 29 H, 280; $C_5Me_5(C_5Me_4CH_2)$),9.4 (m, 1 H, 280; C_5H_3MeN), 7.5 (m, 2 H, 170; C_5H_3MeN), 2.7 (s, 3 H, 50; C_5H_3MeN); IR (KBr/Nujol): $\tilde{\nu} = 2720$, 1596, 1565, 1475, 1450, 1415, 1370, 1310, 1265, 1225, 1210, 1195, 1160, 1102, 1055, 1015, 990, 925, 895, 835, 785, 728, 680, 610, 575, 437, 395 cm^{-1}.
[6] Cell data: $a = 10.045(4)$, $b = 19.333(5)$, $c = 11.504(4)$ Å, $\beta = 96.45(3)°$, $V = 2220.2$ Å^3, $\rho_{calcd} = 1.228$ g cm^{-3}, $\mu = 3.9$ cm^{-1}, $Z = 4$, $P2_1/n$, 4818 unique reflections, 2827 reflections with $I \geq 3\,\sigma(I)$, 398 parameters refined, $R = 0.052$, $R_w = 0.057$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the depository number CSD-52363, the names of the authors, and the journal citation.
[7] a) R. G. Teller, R. Bau, *Struct. Bonding (Berlin) 44* (1981) 1; b) J. A. Jensen, G. S. Girolami, *J. Chem. Soc. Chem. Commun. 1986,* 1160.
[8] F. van Bolhuis, E. J. M. de Boer, J. H. Teuben, *J. Organomet. Chem. 170* (1979) 299.
[9] a) T. C. McKenzie, R. D. Sanner, J. E. Bercaw, *J. Organomet. Chem. 102* (1975) 475; b) S. A. Cohen, P. R. Auburn, J. E. Bercaw, *J. Am. Chem. Soc. 105* (1983) 1136; c) R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, J. E. Bercaw, *ibid. 98* (1976) 8358.
[10] K. H. den Haan, J. L. de Boer, J. H. Teuben, A. L. Spek, B. Kojić-Prodić, G. R. Hays, R. Huis, *Organometallics 5* (1986) 1726.
[11] J. H. Teuben et al., unpublished results.
[12] E. Klei, J. H. Teuben, *J. Organomet. Chem. 214* (1981) 53.
[13] M. E. Thompson, J. E. Bercaw, *Pure Appl. Chem. 56* (1984) 1.
[14] K. H. den Haan, Y. Wielstra, J. H. Teuben, *Organometallics,* in press.
[15] P. L. Watson, *J. Chem. Soc. Chem. Commun. 1983,* 276.